

A Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples

by Stan Feenstra, Douglas M. Mackay, and John A. Cherry

Abstract

Ground water contamination by non-aqueous phase liquid (NAPL) chemicals is a serious concern at many industrial facilities and waste disposal sites. NAPL in the form of immobile residual contamination, or pools of mobile or potentially mobile NAPL, can represent continuing sources of ground water contamination. In order to develop rational and cost-effective plans for remediation of soil and ground water contamination at such sites, it is essential to determine if non-aqueous phase liquid (NAPL) chemicals are present in the subsurface and delineate the zones of NAPL contamination. The presence of NAPL pools may be evident as a floating or sinking phase in monitoring wells. The residual NAPL contamination may be identified in soil samples if residual contents are high and contaminated zones in the soil cores are thick. However, visual identification may not be effective if residual contents are low or if the NAPL residual is distributed heterogeneously in the samples. The chemical analysis of soil samples provides a measure of the total chemical concentration in the soil but cannot determine directly whether NAPL is present in the samples. Qualitatively, soil analyses that exhibit chemical concentrations in the percent range or >10,000 mg/kg would generally be considered to indicate the presence of NAPL. However, the results of soil analyses are seldom used in a quantitative manner to assess the possible presence of residual NAPL contamination when chemical concentrations are lower and the presence of NAPL is not obvious. The assessment of the presence of NAPL in soil samples is possible using the results of chemical and physical analyses of the soil, and the fundamental principles of chemical partitioning in unsaturated or saturated soil. The method requires information on the soil of the type typically considered in ground water contamination studies and provides a simple tool for the investigators of chemical spill and waste disposal sites to assess whether soil chemical analyses indicate the presence of residual NAPL in the subsurface.

Introduction

Ground water contamination by organic chemicals such as chlorinated solvents, petroleum fuels, coal tar and creosote is a serious concern at many industrial facilities and waste disposal sites. In their pure form, these chemicals are non-aqueous phase liquids or NAPLs (Mercer and Cohen 1990). NAPL in the form of immobile residual contamination, or pools of mobile or potentially mobile NAPL, can represent continuing sources of ground water contamination unless NAPL zones are removed from the subsurface, isolated from the ground water system, or treated in situ. In order to develop rational and cost-effective plans for remediation of soil and ground water contamination at such sites, it is essential to determine if non-aqueous phase liquid (NAPL) chemicals are present in the subsurface and delineate the zones of NAPL contamination.

At some sites, the presence of NAPL pools is evident by the recovery of NAPL from monitoring wells. Petroleum fuels and chemical products such as benzene and toluene are lighter than water NAPLs (LNAPL) and may comprise floating layers in monitoring wells. Chlorinated solvents, coal tar, creosote, and PCB Aroclors are NAPLs that are more dense than water

(DNAPLs) and may sink to the bottom of monitoring wells. The presence of residual NAPL contamination in soils is assessed typically by visual inspection and chemical analysis of samples from soil borings. Visual identification of NAPL may be possible if residual contents are high and contaminated zones in the soil cores are thick. However, visual identification may not be effective if residual contents are low or if the NAPL residual is distributed heterogeneously in the samples.

The chemical analysis of soil samples provides a measure of the total chemical concentration in the soil. There are currently no soil analysis methods available to directly confirm the presence of residual NAPL in soil samples. Qualitatively, soil analyses that exhibit high chemical concentrations (in the percent range or >10,000 mg/kg) would generally be considered to indicate the presence of NAPL. However, the results of soil analyses are seldom used in a quantitative manner to assess the possible presence of residual NAPL contamination when chemical concentrations are lower and the presence of NAPL is not obvious. This paper describes a method for the assessment of the possible presence of NAPL in soil samples using the results of chemical and physical analysis of the soil, and the fundamental

principles of chemical partitioning in soil. The method requires information on the soil of the type typically gathered in ground water contamination studies: total chemical concentrations, moisture content, porosity, sorption parameters for the chemicals of interest, and physical and chemical properties of the chemicals of interest. The method is intended to be a simple tool to allow the investigators of chemical spill and waste disposal sites to assess whether soil chemical analyses indicate the presence of residual NAPL in the subsurface.

Methodology

Theory

The chemical analysis of a soil sample for organic compounds involves extraction of the compounds from the sample by either water leaching, solvent leaching, or heating. The analysis generally provides a measure of the total amount of the chemical of interest in the sample, expressed typically as mass of chemical per unit dry weight of the soil sample. The analysis includes the chemical dissolved in the pore water of the sample, sorbed on the soil solids, present in NAPL, and present in the soil gas. The chemical analysis cannot indicate directly how the chemical of interest is distributed between these phases or whether NAPL is present. However, the following describes a method to calculate whether NAPL may be present in a soil sample. The calculations are based on the assumption that no NAPL is present. The apparent pore-water concentration of the constituent of interest is calculated from the measured total soil concentration by assuming equilibrium chemical partitioning between the solid, pore water, and soil-gas phases. With no NAPL present, there is a hypothetical maximum mass of chemical which can be contained in a sample of soil, pore water, and soil gas. The corresponding hypothetical maximum total soil concentration is defined by the solubility of the chemical in water, the saturated soil-gas concentration and the sorption capacity of the solids. If chemical in the form of NAPL is present in a sample, the hypothetical maximum total soil concentration would be exceeded and the calculated pore-water concentration would exceed the solubility of the chemical. The calculations are based on the assumptions of homogeneity of the sample and equilibrium partitioning of chemicals of interest between the pore water, the soil solids, and the soil gas. For typical soil samples of several cubic centimeters or less in volume, this is likely a reasonable assumption. The derivation of the calculations is shown in the following.

The following abbreviations are used in the calculations:

C_t	Total soil chemical concentration ($\mu\text{g/g}$ dry weight)
C_s	Chemical concentration sorbed on the soil solids ($\mu\text{g/g}$ dry weight)
C_w	Chemical concentration in the pore water (mg/L or $\mu\text{g/cm}^3$)
C_a	Chemical concentration in the soil gas (mg/L or $\mu\text{g/cm}^3$)
M_t	Total mass of chemical in soil sample (μg)

M_s	Mass of chemical sorbed on soil solids (μg)
M_w	Mass of chemical in pore water (μg)
M_a	Mass of chemical in soil gas (μg)
ϕ_w	Water-filled porosity (volume fraction)
ϕ_a	Air-filled porosity (volume fraction)
ρ_b	Dry bulk density of the soil sample (g/cm^3)
K_d	Partition coefficient between pore water and soil solids (cm^3/g)
H_c	Dimensionless Henry's Law Constant

The total mass of chemical in the soil sample is:

$$M_t = M_s + M_w + M_a \quad (1)$$

For a 1 cm^3 volume of soil and the units shown above, the following relationships apply:

$$M_s = C_s \rho_b \quad (2)$$

$$M_w = C_w \phi_w \quad (3)$$

$$M_a = C_a \phi_a \quad (4)$$

$$C_t = \frac{M_t}{\rho_b} \quad (5)$$

By substitution of (5) into (1) and rearrangement:

$$C_t = \frac{M_s + M_w + M_a}{\rho_b} \quad (6)$$

By substitution of (2), (3) and (4) into (6):

$$C_t = \frac{C_s \rho_b + C_w \phi_w + C_a \phi_a}{\rho_b} \quad (7)$$

Partitioning between solids and pore water, and soil gas and pore water are described by:

$$K_d = \frac{C_s}{C_w} \quad (8)$$

$$H_c = \frac{C_a}{C_w} \quad (9)$$

By rearrangement of (8) and (9):

$$C_s = K_d C_w \quad (10)$$

$$C_a = C_w H_c \quad (11)$$

By substitution of (10) and (11) into (7):

$$C_t = \frac{K_d C_w \rho_b + C_w \phi_w + C_w H_c \phi_a}{\rho_b} \quad (12)$$

By rearrangement, the pore-water concentration, C_w , can be expressed in terms of the total soil concentration, C_t :

$$C_w = \frac{C_t \rho_b}{(K_d \rho_b + \phi_w + H_c \phi_a)} \quad (13)$$

When sorption is significant, these calculations require that the K_d be constant with concentrations up to the solubility limit and not be affected by competition from other sorbing solutes. While this may be true in some cases, often K_d will decline somewhat for dissolved concentrations exceeding 0.5 of the solubility (Karickhoff 1984). By assuming no dependence of K_d on concentration as is done, it is at worst overestimating K_d and thus the technique might mistake slight concentrations of NAPL as no NAPL, an error of little probable significance. The same type of error may result from assuming no competition between sorbing solutes.

Equation 13 can be simplified in some circumstances. Inherent in Equation 13 is the assumption that the measured total chemical concentration includes the mass of chemical that was present in the soil gas of the sample. However, depending on how the soil sample was collected and handled prior to analysis, much of the chemical mass present in the soil gas may have been lost. In such a situation, the $H_c \phi_a$ term in Equation 13 could be neglected. Similarly, for the consideration of water-saturated soils from the ground water zone (i.e., low air-filled porosity) or for compounds having a very low Henry's Law Constant, the $H_c \phi_a$ term in Equation 13 will approach zero and the equation can then be reduced to:

$$C_w = \frac{C_t \rho_b}{(K_d \rho_b + \phi_w)} \quad (14)$$

Similarly, for the situation where the compounds of interest are not significantly sorbed on the soil solids, the $K_d \rho_b$ term becomes zero and Equation 14 can be further reduced to:

$$C_w = \frac{C_t \rho_b}{\phi_w} \quad (15)$$

The soil concentration used in these equations should be the total concentration determined by an analysis involving removal of the chemicals from the sample by solvent extraction or heating. Analysis following extraction using water or the analysis of headspace gases may not reflect the total chemical concentration because a significant portion of the chemical may remain sorbed on the soil solids depending on the compound of interest and the nature of the sample. Results of this calculation method are directly dependent on the accuracy of the soil analysis. For volatile organics, it is necessary that procedures for sampling and analysis of the samples minimize loss of volatile constituents during collection, handling, and storage prior to analysis.

The use of these equations requires measurements or estimates of parameters related to the properties of the soil and the chemical compounds of interest. Soil parameters such as the dry bulk density, water-filled porosity, and air-filled porosity can be determined from standard measurements of soil density and water content which are performed for most soils investigations. Even in circumstances in which soil porosity and density

must be estimated rather than measured, the possible range in porosity and density values is relatively small and the uncertainty imparted to the calculated pore-water concentrations will be correspondingly small. Henry's Law Constants for most organic compounds of environmental interest can be obtained from published data such as those found in recent compilations by Montgomery and Welkom (1990), Howard (1989), and Howard (1990).

If measured values of K_d are available from batch or column laboratory experiments for the soil and chemicals of interest, such values should be used. However, in the vast majority of situations it will be necessary to estimate appropriate values for K_d . The chemicals of most interest with regard to ground water contamination, such as chlorinated solvents and BTEX compounds (benzene, toluene, ethylbenzene, xylenes), are non-polar organics. The sorption of non-polar organics on soils is predominantly the result of partitioning of the dissolved chemicals from the ground water onto the solid organic materials in the soil provided the organic carbon content is greater than 0.1 percent as a general rule (Karickhoff 1984). The degree of sorption is defined by:

$$K_d = K_{oc} f_{oc} \quad (16)$$

where K_{oc} is the organic carbon-water partition coefficient for the chemical of interest and f_{oc} is the fraction of organic carbon in the soil. Values for K_{oc} can be obtained from published data such as those found in recent compilations by Montgomery and Welkom (1990). Values for f_{oc} can be measured by laboratory analysis of the soil. In some circumstances, factors such as differences in the nature of the soil organic material, sorption on mineral surfaces, dissolved chemical concentrations in the ground water approaching solubility values, and the presence of dissolved organic matter or cosolvents in the ground water may cause this relationship to be in error. Equation 16 still provides the only general means of estimating K_d values without direct measurement. In general, the largest uncertainty in the pore-water concentrations calculated by Equation 13 will be imparted by uncertainty in the estimation of representative K_d values.

Equations 14 and 15 should be used only when the simplifying assumptions are appropriate. For the most common organic contaminants in ground water, such as trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, benzene, toluene, ethylbenzene and xylenes, the $K_d \rho_b$ and $H_c \phi_a$ terms in Equation 13 should not be neglected. Consider, for example, trichloroethylene (TCE) in a sample of partially water-saturated soil with the parameters: $\phi_w = 0.1$; $\phi_a = 0.2$; $\rho_b = 1.86 \text{ g/cm}^3$; $f_{oc} = 0.001$, and $C_t = 100 \text{ mg/kg}$. TCE has a Henry's Law Constant of 0.163 at 9.6 C (Gossett 1987) and a K_{oc} of 126 (Schwille 1988). When these parameter values are used in Equation 15 and sorption on soil solids and partitioning into soil gas is neglected, the calculated pore-water concentration is 1860 mg/L. This concentra-

tion exceeds 1100 mg/L, the solubility of TCE, and would lead to the conclusion that NAPL TCE is present in the soil sample. When Equation 14 is used, sorption on soil solids is accounted for and only partitioning into soil gas is neglected. In this case, the calculated pore-water concentration is 560 mg/L. This concentration does not exceed the solubility of TCE and would not lead to the conclusion that NAPL TCE is present in the sample. When Equation 13 is used and both sorption and soil-gas partitioning are accounted for, the calculated pore-water concentration is 510 mg/L. From this example it is clear that neglecting sorption and soil-gas partitioning is not an appropriate assumption and may lead to incorrect conclusions regarding the presence of NAPL.

Solubility and Effective Solubility

To apply the equations in the preceding section to evaluating the presence of NAPL in soil samples, it is necessary to have information on the water solubility of the compounds of interest. LNAPL and DNAPL can be comprised of single component liquid chemicals, mixtures of liquid chemicals, or multicomponent mixtures of liquids and dissolved solid-phase organics. Chlorinated solvents and BTEX compounds are liquid chemicals in their pure form at subsurface temperatures (0 C to 25 C) and exhibit a wide range in solubility (see Table 1).

TABLE 1
Water Solubility of Common Organic
Chemical Contaminants at 25 C

(Data for chlorinated solvents from Horvath (1982) and data for BTEX compounds from Miller et al. (1985). Solubility data rounded to two significant figures.)

Chemical	Solubility in Water (mg/L)
Methylene chloride	13,000
1,2-Dichloroethane	8600
Benzene	1800
Trichloroethylene	1100
Toluene	580
o-Xylene	220
m-Xylene	160
p-Xylene	210
Ethylbenzene	190
Tetrachloroethylene	150

For mixtures of liquid chemicals, the dissolved-phase concentrations in equilibrium with the NAPL mixture can be estimated by:

$$S_i^c = X_i S_i \quad (17)$$

where S_i^c is the dissolved-phase concentration or effective solubility of compound i , X_i is the mole fraction of the compound i in the NAPL mixture, and S_i is the pure-phase solubility of compound i (Shiu et al. 1988). Strictly, this relationship is correct only for ideal liquid mixtures. Laboratory experimental studies (Banerjee

1984) suggest that this relationship is a reasonable approximation for mixtures of structurally related hydrophobic organic liquids. Other laboratory studies (Leinonen et al. 1973) have shown that the estimation of effective solubility by this relationship may be in error for complex mixtures such as petroleum hydrocarbons, but the error is unlikely to be greater than a factor of two. With estimates of the effective solubility it is possible to compare the effective solubility of components of a multicomponent NAPL to the pore-water concentrations of the components calculated by Equation 13. If the calculated pore-water concentrations exceed the effective solubilities, it can be concluded that NAPL may be present in the soil sample. For the purpose of these calculations, the uncertainty in effective solubility imparted by using Equation 17 will not be unacceptably high in most circumstances. Exceptions would be sites where miscible co-solvents such as surfactants, alcohols, or ketones are present in the ground water at high concentrations. In such cases, the co-solvents may significantly increase the effective solubility of the NAPL components (Rao et al. 1985; Kile and Chiou 1989).

An alternate approach would be to equilibrate NAPL with uncontaminated ground water from the site to attempt to directly measure the effective solubility of the components in the ground water. The use of measured values for effective solubility would avoid the uncertainty imparted by the use of Equation 13. However, this type of testing requires particular care to prevent the formation of emulsions of NAPL in the water which will yield erroneously high dissolved concentrations (Billington et al. 1988).

NAPL encountered at many waste disposal sites and chemicals such as coal tar, creosote, and PCB Aroclors are liquids, but are comprised of many compounds which, in their pure form, are solids at subsurface temperatures (0 C to 25 C). The solubility data reported in the literature for such compounds are generally those of the pure solid compound in contact with water. This solid-phase solubility is not the appropriate value to use in the estimation of the effective solubility of such compounds when they are dissolved in a NAPL (Shiu et al. 1988). In such a case, the liquid-phase solubility of the compound should be used.

Liquid-phase solubility values for such compounds can be estimated based on the solid-phase solubility of the compound, the melting point of the compound and the temperature (Shiu et al. 1988). Liquid-phase and solid-phase solubility values for a variety of hydrocarbons and chlorinated hydrocarbons, which are of interest in soils and ground water, are tabulated by Miller et al. (1985) and Eastcott et al. (1988). The liquid-phase solubility values can be considerably higher than solid-phase solubility values; the difference is greater for compounds having higher melting points (see Table 2).

The calculation of the effective solubilities of the components of a multicomponent NAPL requires suitable values of the liquid-phase solubilities of the components and information on the chemical composition of the NAPL. Ideally, the complete chemical composition

TABLE 2
Melting Points and Water Solubilities (25 C) of Several Key Constituents
of Creosote and Coal Tar

(Data from Miller et al. (1985). Solubility data rounded to two significant figures.)

Compound	Melting Point (°C)	Solubility (mg/L)	
		Solid-Phase	Liquid-Phase
Naphthalene	80.2	31	100
Fluorene	117	1.8	12
Anthracene	217	0.73	7.1
Benzo(a)pyrene	179	0.0038	0.12

TABLE 3
Calculated Effective Solubility for Components of a DNAPL from a Superfund Site
in Pennsylvania for Different Assumed Molecular Masses for the Unidentified Fraction

	Wt. %	MM (g/mol)	C _L (mg/L)	Effective Solubility (mg/L)		
				Assumed MM of Unidentified Fraction		
				MM-100	MM-200	MM-300
1,2,3-Trichloropropane	23	146.4	1900	325	450	520
Toluene	4.2	92.1	580	29	40	46
Xylenes	17	106.2	200	33	46	53
Ethylbenzene	3.8	106.2	190	7.4	10	12
Unidentified	52					

MM-Molecular mass.

of the NAPL can be determined by analysis of samples of NAPL recovered from the subsurface. In the case of petroleum fuel spills, there may be suitable information on the chemical composition of the product without analysis of NAPL recovered from the subsurface. However, at many waste disposal and chemical spill sites, the NAPL contains a substantial proportion of organic compounds that cannot be identified and quantified by standard analytical methods, or samples of NAPL are not available for analysis. In these situations, assumptions must be made regarding the composition of the NAPL.

For the case in which there is an unidentified fraction of the NAPL, an average molecular mass must be assumed for the unidentified fraction to allow calculation of the mole fractions of the identified components. If the molecular mass assumed for the unidentified fraction is erroneously high, the calculated effective solubility values for the components of interest will also be erroneously high. This is the case because for a given weight percent of unidentified fraction, a higher assumed molecular mass will result in a lower calculated mole fraction for the unidentified fraction and correspondingly higher mole fractions for the identified components. This effect is illustrated by effective solubility calculations for a DNAPL from a Superfund site in Pennsylvania shown in Table 3. The potential error in assumption of the molecular mass of the unidentified fraction is probably less than a factor of two for most NAPL mixtures because at most sites there is some prior knowledge of the nature of the chemical mixture.

For cases where samples of NAPL can be recovered from a site, the chemical analysis of the NAPL can be used to estimate the effective solubility of the components as described previously. In the case where samples of NAPL are not available for chemical analysis, it may be possible to use the chemical analysis of soil samples that exhibit visual evidence of NAPL or are highly contaminated (thousands of mg/kg or more) to estimate the composition of the NAPL. This could then be used as a basis to evaluate the presence of NAPL in less contaminated soil samples.

Example Applications

The following examples illustrate how the results of soil analyses from actual field sites can be used to estimate whether NAPL is present in the subsurface. These examples do not represent verification of the conclusions resulting from the calculations because it is currently not possible to independently confirm whether NAPL is present. For two of the following examples, a generic graph is presented that can be used to relate soil concentrations to the hypothetical pore-water concentration for soils having a range of sorption characteristics. Such graphs can be readily produced for specific chemicals and specific soil conditions using the equations presented in this paper. Such graphs provide useful tools for rapid evaluation of soil analyses from field sites.

Trichloroethylene Leak at an Industrial Site

Soil samples were collected from borings around an

industrial facility in order to assess the source of trichloroethylene (TCE) contamination in the ground water beneath the site. Several of these results are shown in Table 4. The TCE concentrations in these samples range from 3100 mg/kg to 210 mg/kg. These soil samples were all collected from near or below the water table. It is assumed that the dry bulk density is 1.86 g/cm^3 , the total porosity is 0.3 and there is no air-filled porosity. The K_{oc} for TCE reported by Schwille (1988) is 126 and the assumed f_{oc} is 0.001 or 0.1 percent. Using these parameter values and Equation 13, the calculated pore-water concentrations range from 11,000 mg/L to 730 mg/L.

TABLE 4
Results of Trichloroethylene (TCE) Analysis of Soil and Calculation of Hypothetical Pore-Water Concentrations

(Parameters used for calculations:

$\phi_w=0.3$; $\phi_a=0$; $\rho_b=1.86 \text{ g/cm}^3$; $K_{oc}=126$; $f_{oc}=0.001$)

Sample Depth (m)	Measured TCE in Soil (mg/kg)	Calculated Pore-Water Concentration (mg/L)
2.13	3100	11,000
6.10	420	1500
9.14	210	730

TCE was used as a degreasing solvent at this site and no other chemicals were detected in the soil samples at significant concentrations. It is not known whether the TCE released to the subsurface was pure solvent or spent solvent, which may have contained substantial proportions of oil and grease compounds. The effective solubility of TCE in spent solvent mixture would be expected to be somewhat less than the 1100 mg/L solubility of pure-phase TCE. The calculated pore-water concentration for the sample from 2.13m depth greatly exceeds the solubility of TCE and suggests the presence of NAPL TCE in this sample. The calculated pore-water concentrations in the samples from 6.10m and 9.14m depths are slightly greater and slightly lower, respec-

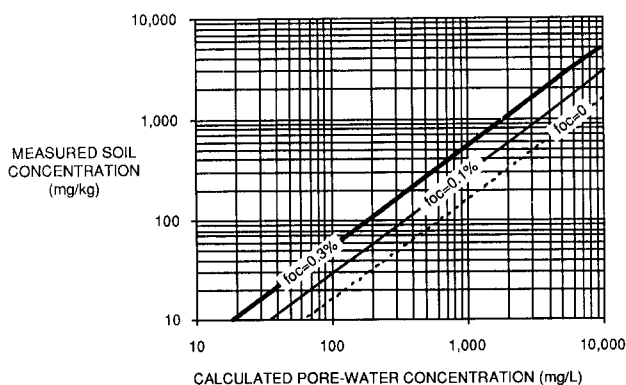


Figure 1. Relationship between measured concentration of TCE in soil and the calculated TCE concentration in the pore water for a generic soil. Parameters used for calculations: $\phi_w=0.3$; $\phi_a=0$; $\rho_b=1.86 \text{ g/cm}^3$; $K_{oc}=126$.

tively, than the pure-phase solubility of TCE. Given the fact that the effective solubility of TCE in a spent solvent may be lower than the pure-phase solubility, these results may also suggest the presence of a small quantity of NAPL TCE in these samples. In this example, any soil concentration above about 300 mg/kg indicates a good possibility that residual NAPL TCE is present in the sample.

A graph relating TCE concentrations in soil to the calculated pore-water concentration is shown in Figure 1. This graph is a generic one for a typical water-saturated soil having a ϕ_w of 0.3 and a ρ_b of 1.86 g/cm^3 . Three lines are shown representing soils having f_{oc} values of 0.3 percent, 0.1 percent, and 0, the range that would be expected in most natural subsurface soils. For a given soil concentration, the calculated pore-water concentration is lower for higher values of f_{oc} because a larger proportion of the chemical mass is sorbed on the soil solids.

Gasoline Leak at a Fuels Marketing Area

Soil samples were collected from borings around a petroleum fuels marketing area where gasoline leaked to the subsurface. BTX (benzene, toluene, xylenes) analyses for several of these samples are shown in Table 5. It is assumed that the dry bulk density is 1.86 g/cm^3 , the total porosity is 0.3 and there is no air-filled porosity. The K_{oc} values for benzene, toluene, and xylenes

TABLE 5
Results of BTX Analyses of Soil and Calculation of Hypothetical Pore-Water Concentrations

(Parameters used for calculations: $\phi_w=0.3$; $\phi_a=0$; $\rho_b=1.86 \text{ g/cm}^3$; $f_{oc}=0.0003$; K_{oc} values = 49, 155 and 630 for benzene, toluene and xylenes, respectively.)

Sample		Measured Conc. in Soil (mg/kg)	Calculated Pore-Water Conc. (mg/L)	Effective Solubility (mg/L)
1	Benzene	5.6	32	36
	Toluene	50.8	260	87
	Xylenes	255	730	20
2	Benzene	3.3	19	36
	Toluene	290	1500	87
	Xylenes	450	1300	20

reported by Abdul et al. (1987) are 49, 115, and 630, respectively. The soil is sandy and the f_{oc} is assumed to be 0.0003 or 0.03 percent. Using these parameter values and Equation 17, the pore-water concentrations were calculated and are shown in Table 5.

The chemical composition of the gasoline in the subsurface was not determined specifically so the NAPL composition must be estimated. The composition of gasoline varies between manufacturers, with gasoline grade, and with the season in which it is marketed. In addition, weathering processes in the subsurface such as evaporation and dissolution can alter the chemical composition of the gasoline from that which was released. Weathered gasoline may be depleted in the more volatile and more soluble compounds (i.e., benzene and toluene). These uncertainties in composition must be recognized when the NAPL composition cannot be measured and must be estimated.

For the purpose of the calculations considered here, the gasoline is assumed to have a composition similar to fresh gasoline. Typical BTEX levels in fresh premium-grade gasoline might be approximately 2 percent benzene, 15 percent toluene, 2 percent ethylbenzene, and 10 percent xylenes (Kreamer and Stetzenbach 1990). The average molecular mass of the remaining components in gasoline is similar to the molecular masses of BTEX compounds so that mole fractions of the BTEX compounds can be approximated reasonably by the weight percent composition. With these data and the pure-phase solubilities of the BTEX compounds (see Table 1), effective solubilities of 36 mg/L, 87 mg/L, and 20 mg/L are calculated for benzene, toluene and xylenes, respectively.

For both soil samples, the calculated pore-water concentrations for toluene and xylenes greatly exceed the estimated effective solubility values. This suggests that NAPL gasoline is present in these samples. However, the calculated pore-water concentrations for benzene approach, but do not exceed, the effective solubility. The calculations for benzene are much less convincing for the presence of NAPL gasoline in these samples. This may be the result of differences between the actual gasoline composition and the composition assumed for these calculations, or the preferential loss of benzene by weathering processes in the soil. For multicomponent NAPL where the composition must be estimated, it would be wise to perform pore-water concentration calculations for several components and base conclusions regarding the presence of NAPL on the overall results for the suite of components rather than an individual component.

PCB-Contaminated Hydrocarbons at an Industrial Site

Soil samples were collected from borings around disposal pits in which PCB (polychlorinated biphenyl) – contaminated hydrocarbon liquids were released. Several of these results are shown in Table 6. The total PCB concentrations in these samples range from 590 mg/kg to 71 mg/kg and the PCBs were identified to resemble Aroclor 1248. These soil samples were all col-

TABLE 6
Results of PCB Analyses of Soil and
Calculation of Hypothetical Pore-Water
Concentrations

(Parameters used for calculations: $\phi_w=0.3$; $\phi_a=0$; $\rho_b=1.86$ g/cm³; $K_{oc}=54,626$; $f_{oc}=0.003$)

Sample Depth (m)	Measured PCB in Soil (mg/kg)	Calculated Pore-Water Concentration (μg/L)
0.63	590	1600
0.91	310	860
1.04	170	470
1.77	71	200

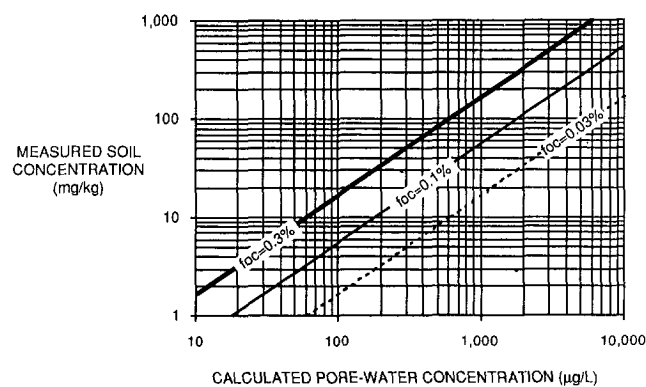


Figure 2. Relationship between measured concentration of PCB Aroclor 1248 in soil and the calculated PCB concentration in the pore water for a generic soil. Parameters used for calculations: $\phi_w=0.3$; $\phi_a=0$; $\rho_b=1.86$ g/cm³; $K_{oc}=54,626$.

lected from near or below the water table. It is assumed that the dry bulk density is 1.86 g/cm³, the total porosity is 0.3 and there is no air-filled porosity. The K_{oc} for Aroclor 1248 reported by Chou and Griffin (1986) is 54,626 and the assumed f_{oc} is 0.003 or 0.3 percent. Using these parameter values and Equation 13, the calculated pore-water concentrations range from 3600 μg/L to 430 μg/L.

PCB was a contaminant in the hydrocarbon liquids released to the subsurface and was believed to be present in concentrations up to 5 percent. The overall chemical composition of the hydrocarbon mixture is not known so it is assumed that the mole fraction of PCB in the hydrocarbon mixture is approximately 5 percent also. The estimated effective solubility of PCB in the hydrocarbon mixture would be 5 percent of the pure-phase solubility of 54 μg/L for Aroclor 1248 (Chou and Griffin 1986), or 2.7 μg/L. All of the calculated pore-water concentrations greatly exceed the estimated effective solubility and the pure-phase solubility for Aroclor 1248, indicating the presence of NAPL in all the samples analyzed.

A graph relating PCB concentrations in soil to the calculated pore-water concentration is shown in Figure 2. This graph is a generic one for a typical water-saturated soil having a ϕ_w of 0.3 and a ρ_b of 1.86 g/cm³.

Three lines are shown representing soils having f_{oc} values of 0.3 percent, 0.1 percent, and 0.03 percent, the range that would be expected in most natural subsurface soils. For a given soil concentration, the calculated pore-water concentration is lower for higher values of f_{oc} because a larger proportion of the chemical mass is sorbed on the soil solids. It is also evident that the effect of sorption on the calculated pore-water concentrations is greater for strongly sorbed compounds such as PCBs compared to compounds such as TCE or toluene.

Conclusion

This method is intended to be a simple tool to allow the investigators of chemical spill and waste disposal sites to address whether soil chemical analyses indicate the presence of residual NAPL in the subsurface. The method requires information on the soil of the type typically gathered in ground water contamination studies: total chemical concentrations, moisture content, porosity, sorption parameters for the chemicals of interest, and physical and chemical properties of the chemicals of interest. Conclusions regarding the presence of NAPL in soil samples are most reliable for cases where significant residual NAPL is present; the pore water-soil partition coefficients can be measured for the compounds of interest; and for single component or multi-component NAPL for which the effective solubility of the components can be measured. The conclusions on the presence of NAPL are less reliable when parameters such as sorption coefficients and effective solubility must be estimated. However, at the present time calculations such as this provide the only method for the assessment of the presence of residual NAPL in soil samples until laboratory analysis methods are developed which can confirm the presence of low levels of NAPL contamination directly.

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Biographical Sketches

Stan Feenstra is a hydrogeochemist and president of Applied Groundwater Research Ltd. in Mississauga, Ontario. He received a B.Sc. in earth sciences and an M.Sc. in hydrogeology from the University of Waterloo in 1978 and 1980, respectively, and was designated a Certified Ground Water Professional by AGWSE in 1989. Since 1980, he has been a ground water consultant with Golder Associates in Mississauga, Ontario, and Zenon Environmental in Burlington, Ontario, and founded Applied Groundwater Research Ltd. in 1987. Feenstra specializes in the hydrogeochemical evaluation of ground water contamination at waste disposal facilities and chemical spill sites. He is currently a Ph.D. candidate in hydrogeology and research associate in the Waterloo Centre for Ground Water Research at the University of Waterloo (Waterloo, Ontario N2L 3G1) and is involved in research related to the behavior of dense organic solvents in ground water.

Douglas M. Mackay is an adjunct professor at the Waterloo Centre for Groundwater Research at the University of Waterloo, Waterloo, Ontario (N2L 3G1). Dr. Mackay received a B.S. in engineering and M.S. and Ph.D. in civil engineering from Stanford University in 1970, 1973, and 1981, respectively. From 1986 to 1990, he was a faculty member of the Environmental Science and Engineering Program of the UCLA School of Public Health. His research focuses on field studies of transport and fate of organic chemicals in ground water, various scale studies of decontamination of soil and ground water, and ground water monitoring technologies.

John A. Cherry is a professor at the Waterloo Centre for Groundwater Research at the University of Waterloo, Waterloo, Ontario (N2L 3G1). He received his B.S. in geological engineering from the University of Saskatchewan in 1962. He received his M.S. from the University of California at Berkeley in 1964, and his Ph.D. from the Department of Geology at the University of Illinois in 1966. His research interests include the field study and modeling of contaminants in ground water systems, as well as the development of monitoring techniques for the study of ground water contaminants.

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